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COMPLETE SPECIFICATION

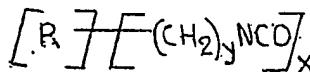
Treating Materials with Polyisocyanates

We, GENERAL MILLS INC., of 9200 Wayzata Boulevard, Minneapolis, Minnesota 55440, United States of America, a corporation organised under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the treatment of fibrous materials and leather with polyisocyanates and to the products so treated.

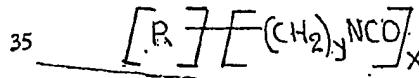
It has previously been proposed to treat fibrous materials in order to modify certain physical characteristics thereof such as softness, water repellency, crease resistance and tear resistance. It has now been found that the properties of fibrous materials can be improved by treating the fibrous materials with certain polyisocyanates.

According to the present invention there is provided a process of treating a fibrous material or leather which comprises contacting the fibrous material or leather with a compound having the formula:



where y is 0 or 1, x is 2, 3 or 4 and R is the hydrocarbon radical of a polymeric fat acid, as herein defined.

The polyisocyanates employed in the process of the present invention are described and claimed in Patent No. 1,023,390 and having the following idealized, structural formula:



where y is 0 or 1, x is 2, 3 or 4 and R is the hydrocarbon radical of a polymeric fat acid as therein defined. Advantageously the polyisocyanates used in the present invention will be those in which x is 2.

The polyisocyanates may be prepared by the methods described in Patent No. 1,023,390. The polymeric fat acids, useful as the starting materials for preparing our polyisocyanates are prepared by polymerizing a fat acid as described in Patent No. 1,023,390. The term "fat acid" as used herein refers to naturally occurring and synthetic monobasic aliphatic or cycloaliphatic carboxylic acids having hydrocarbon radicals of 8—24 carbon atoms. The term "fat acids", therefore, includes saturated, ethylenically unsaturated and acetylenically unsaturated acids. It is however preferred, for commercial reasons to employ ethylenically unsaturated acids such as the mixture of oleic and linoleic acids which occurs as tall oil fatty acids. "Polymeric fat radical" is generic to the divalent, trivalent and polyvalent hydrocarbon radicals of dimerized fat acids, trimerized fat acids and higher polymers of fat acids, respectively. These divalent and trivalent radicals are referred to herein as "dimeric fat radical" and "trimeric fat radical".

The isocyanates described above may be used to treat a wide variety of fibrous material and leathers. The fibrous materials are principally cellulosic in nature, although the process of the invention may also be used for the treatment of non-cellulosic fibres, such as wool and other animal fibres as well as synthetic cellulosic and noncellulosic fibres, such as viscose rayon, cuprammonium rayon, cellulose acetate, nylon and polyester fibres, and also mixtures of fibres such as mixtures of cotton and polyester fibres. The process of the invention is applicable to the treatment of woven textile materials from the above sources as well as fibrous sheets, pads and films laid down from such fibres even though in a non-woven form. It is also

applicable to other forms of the fibres as, for example, cellulose sponge.

The isocyanates may be used to treat leather products in general. This includes the leather from any animal and particularly the readily available leathers such as those derived from cow hide, pig skin, goat skin or horse hide. The leather may be ordinary tanned leather or it may have been subjected to additional finishing operations.

The nature of the reaction, if any, between the fibrous material or leather and the isocyanate is not known.

In the case of fibrous materials it is, of course, possible that the isocyanate groups may react with hydroxyl groups or other functional groups in the cellulosic molecule and may react with amine groups or other functional groups in noncellulosic fibrous materials, such as wool. It is also possible that the action which is obtained by the treatment of the isocyanate with the fibrous material is physical in nature. A further possibility is that the isocyanates may form homopolymers through reaction between water and the isocyanate groups to form polyureas. Regardless of what the physical or chemical action is which takes place, it has been observed that the treatment of the fibrous material with the isocyanates does modify the physical properties of the fibrous material. This modification may be in any of a number of ways, including softening, water repellency, wrinkle resistance and tear resistance.

In the case of leather the isocyanate groups may possibly react with the various functional groups in leather, such as the amine and amide groups. It is also possible that the phenomenon observed may be entirely physical. However, from data hereinafter presented, it is believed that there is an actual reaction between leather and the polyisocyanate. Following the application of the polyisocyanate to leather, curing is allowed to take place. This may be accomplished either at room temperature or at elevated temperatures. The time period at room temperature is, of course, extended as compared with that at elevated temperature. It is generally preferred to avoid curing temperatures in excess of 100° C. because of the deleterious effect of such higher temperatures on certain types of leather. The treatment of leather with these polyisocyanates has the effect of rendering the leather water repellent while at the same time not adversely affecting any of the other desirable natural properties of the leather, e.g. flexibility, and breathability. The diisocyanates also have certain bacteriocidal properties which make them useful as a non-toxic preservative for cotton. This treatment provides some protection against microbiological attack in soil burial tests. The treated material is relatively non-toxic as compared to other bacteriocides commonly used for this purpose, such as copper naphthenate.

The process of treating the fibrous material or leather can be effected in any of a number of ways. The polyisocyanates of the present invention are generally liquid in nature, and accordingly, may be simply applied as a hundred percent material. As an alternative the polyisocyanate may be dissolved in a suitable organic solvent and the solution thus obtained applied to the fibrous material or leather. It is sometimes preferred, however, to emulsify the polymeric fat polyisocyanate in an aqueous system and then treat the fibrous material or leather with the aqueous emulsion. The polymeric fat acid isocyanate is very slowly reactive toward water and, accordingly, there is no great loss of isocyanate groups in the limited period of time that aqueous emulsion is formed and applied to the fibrous material or leather. The application of the polyisocyanate to the fibrous material or leather may be accomplished by immersion, brushing or spraying. It is possible to completely impregnate the fibrous material or leather product with the polyisocyanate or to apply only a surface coating which in the case of treating leather has the effect of modifying the characteristics of the surface portion of the leather or a limited thickness of the leather.

A wide variety of solvents, for example benzene, toluene, hexane or heptane may be used for the application of the isocyanates to the fibrous material or leather. Similarly, a wide variety of emulsions and emulsifying agents may be used. Relatively small quantities of the isocyanates are effective to modify properties somewhat. The degree to which the properties are modified depends to some extent on the concentration of the isocyanate employed. In general, even minute quantities of the isocyanates produce some results.

In general, and in particular for the purposes of softening fibrous materials quantities of 0.1% by weight and above should be used and for water repellency or water proofing, higher levels of 1% by weight or up to 5 and, in some instances, even 10% may be used. Good results are obtainable at relatively two levels for both softening and water repellency as indicated by the examples. The higher levels may be desirable where especially high degrees of water repellency or water proofness are desired.

When treating leather the quantity of polyisocyanate employed can also be varied over considerable limits. In general, even small quantities of polyisocyanate contribute some modification of the water repellency property of leather but, in general, and in particular for treating leather, it is preferred to employ at least one quarter of one percent by weight based on the weight of the leather, and preferably, not in excess of five percent of the weight of the leather. Larger quantities, of course, can be used and by reason of the hydrophobic character of the polyisocyanates

contribute some additional water repellency even though there may not be any reaction of such excess polyisocyanate with the leather. In general, the quantity of polyisocyanate which reacts with the leather is five percent or less. 5

The following examples will serve to illustrate the invention. In these examples, the polyisocyanate, which is referred to as dimethyl isocyanate, which is the diisocyanate prepared from essentially pure dimeric fatty acid, which, in turn is derived from the dimerization of linoleic acid. In this particular instance, the isocyanate was formed via the phosgene route. 10

All percentages referred to in the Examples are by weight. 15

EXAMPLE 1

Birdseye cotton was agitated for 1 min. in a 1% dimethyl isocyanate solution using benzene as the solvent. The treated cotton was wrung out by hand to a 150% wet pickup and then cured for 15 min. at 90—100° C. After curing the treated swatch was rinsed in warm tap water and again dried at 90—100° C. The treated swatch was soft and was very water repellent. After washing with Tide (registered Trade Mark), detergent, the treated samples were still soft and water repellent. Water dropped on the treated cloth after washing or extraction stayed there indefinitely without soaking in. 20

EXAMPLE 2

Birdseye cotton was agitated for 1 min. in 0.5 and 1.0% aqueous dispersions of dimethyl isocyanate. These dispersions were prepared by mixing for 1 min. in a Waring Blender using 0.2% Triton (registered Trade Mark) X—114 (Rohm & Haas U.S.A.) [reaction product of *t*-octylphenol and ethylene oxide (avg. of 7—8 moles)] as an emulsifying agent. The treated cotton was wrung out to a 100% wet pickup and cured for 15 min. at 90—100° C. After curing the treated swatches were rinsed in warm tap water and again dried at 90—100° C. The treated samples were soft and very water repellent. After extraction with hot acetone for 6 min. the treated samples were still very water repellent. Water dropped on the treated cloth after extraction stayed there indefinitely without soaking in. 25

EXAMPLE 3

Birdseye cotton was treated for 1 min. in 0.5, 1.0 and 2.0% aqueous dispersions of dimethyl isocyanate and, for comparative purposes, with the corresponding amounts of corresponding concentration aqueous dispersions of octadecyl isocyanate. These dispersions were prepared by mixing for 1 min. in a Waring Blender using 0.2% Triton X—114 (Rohm & Haas U.S.A.) as an emulsifying agent and 5% acetone as a carrier solvent for the isocyanates. The treated cotton was wrung out to an approximate 100% wet pickup and cured for 20 min. at 90—100° C. After curing the 30

treated swatches were rinsed in warm water using a Kenmore (registered Trade Mark) automatic washer and again dried for 20 min. at 90—100° C. 65

Dimethyl isocyanate samples were subjected to an 8 hour extraction in a Soxhlet extractor using acetone as the solvent. After 8 hours extraction the samples were rinsed in warm tap water and allowed to dry at room temperature. All samples were still very water repellent even at the 0.5% treatment level. Water dropped on the treated cloth after extraction stayed there indefinitely without soaking in. 70

Additional specimens of the above-treated cotton (not subjected to the Soxhlet extraction) were subjected to repeated washing in Tide detergent to determine the permanency of the water repellency and effect on softening. After 15 washes the dimethyl isocyanate treated cotton was still water repellent with the 0.5% treatment level showing some wetting if subjected to long contact with water. After 15 washes octadecyl isocyanate-treated cotton showed loss of water repellency at the 0.5% treatment level where water soaped in immediately on contact and at the 1.0 and 2.0% treatment levels where wetting occurred on longer contact times. 75

EXAMPLE 4

Waterproofing of paper. 80

A 1% emulsion of dimethyl isocyanate in water was prepared. Pieces of paper towels were dipped in this emulsion and then dried in an air-circulating oven at 100—110° C. Other pieces of the same paper were treated with plain water and dried in the same manner. The paper treated with the dimethyl isocyanate showed a definite waterproofing effect. 90

EXAMPLE 5

A series of softening tests were run to compare the softening effect of dimethyl isocyanate, octadecyl isocyanate and a commercial softener, a difatty quaternary ammonium compound, commonly used in conventional laundry softening compositions. The dimethyl isocyanate and the octadecyl isocyanate were applied to the fabric by the method described in Example 2, including the curing and drying step. The fatty quaternary ammonium compound was used as a softening rinse following the laundering operation, in the typical manner in which these laundry rinses are customarily used. These laundry rinses are customarily used at a level of 0.125% softening solids based on the weight of the fabric and the fatty quaternary ammonium compound was so used in this test. With reference to the isocyanates, one set of tests was conducted at this 0.125% level and another set at the 0.25% level. The samples treated with the dimethyl isocyanate and octadecyl isocyanate were given only one treatment and then were subjected to 26 washes without retreatment. The samples softness test by a panel of women. The num- 95

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5 treated with the fatty quaternary ammonium compound were likewise subjected to 26 washes but were given the softening treatment following each washing (at the 0.125% level in all tests). The specimens of cotton thus treated were suitably coded and then subjected to a

10 numbers in the following table indicate the number of times the indicated sample of each pair was chosen as being softer out of 24 tests. The small numbers in parenthesis indicate the statistical significance level of the test (N.S. equals "not significant").

TABLE I

| 0.125% Level 1 Wash | 15 Washes | 26 Washes |
|------------------------|---------------------|---------------------|
| A-19 vs. B- 5(0.01) | A-17 vs. B- 7(0.05) | A-16 vs. B- 8(N.S.) |
| A- 4 vs. C-20(0.01) | A- 4 vs. C-20(0.01) | A- 8 vs. C-16(N.S.) |
| A-24 vs. D- 0(0.01) | A-20 vs. D- 4(0.01) | A-24 vs. D- 0(0.01) |
| 0.25% Level 1 Wash | 15 Washes | 26 Washes |
| A-18 vs. B- 6(0.025) | A-21 vs. B- 3(0.01) | A-17 vs. B- 7(0.05) |
| A-13 vs. C-11(N.S.) | A- 7 vs. C-17(0.05) | A- 5 vs. C-19(0.01) |
| A-23 vs. D- 1(0.01) | A-24 vs. D- 0(0.01) | A-24 vs. D- 0(0.01) |

A = dimethyl isocyanate

B = octadecyl isocyanate

C = difatty quaternary ammonium compound (0.125% in all tests)

D = control

15 These results show a highly significant softening at both levels of dimethyl isocyanate after 26 washes. The dimethyl isocyanate appears to be more effective than the octadecyl isocyanate at the same level. The softening effect of the difatty quaternary ammonium compound (0.125% in all tests)

20 appears to be somewhat better but it must be appreciated that this compound was used after each wash whereas the isocyanates were applied only once.

25 Water repellency tests were run on the samples which involved using a modified "rain test" in which water was sprayed on the sample and the amount of absorbed water was measured. In the following table, the figures represent the percent of water absorbed based on the amount of water absorbed by a pre-washed control, washed once, in a non-ionic detergent, as a 100%. The lower value, the 30 more repellent the sample is.

TABLE II

| | 1 Wash | 6 Washes | 15 Washes | 26 Washes |
|--------------|--------|----------|-----------|-----------|
| 0.125% A | 20.3 | 14.1 | 29.7 | 43.7 |
| 0.25% A | 12.5 | 9.4 | 12.5 | 20.3 |
| 0.125% B | 73.5 | — | 94.0 | 94.0 |
| 0.25% B | 12.5 | — | 73.5 | 86.0 |
| Aliquat H226 | 61.0 | 65.6 | 45.3 | 58.9 |
| Control | 84.4 | 87.5 | 81.3 | 90.6 |

35 These results show that even at the low levels at which dimethyl isocyanate was used in the softening test some repellency is still obtained at the end of 26 washes.

40 EXAMPLE 6
45 50 Small pieces of top-grain cowhide leather were soaked in dimethyl isocyanate for four minutes and then placed in an air circulating oven at 55° C. for a period of eighteen

45 minutes. After removal from the oven, the leather samples were pliable and did not seem to have embrittled. Drops of water were placed on the smooth surface of the leather. A sharp contact angle between the water droplets and the surface of the leather was observed. The water droplets stayed on the treated leather for more than six hours. It was also possible to shake these water droplets off the treated leather.

EXAMPLE 7

Different concentrations of dimethyl isocyanate in benzene were prepared. Pieces of top-grain cowhide leather were then placed in these different solutions for a period of two minutes. The treated pieces of leather were then placed in an air-circulating oven preheated to 50° C. for a period of 15 minutes. After curing, the leather was tested for water repellency by measuring the average time required for two drops of water to penetrate into the leather. These same pieces were then stored for six days at room temperature and retested for water repellency. The results of these tests are summarized below.

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| Concentration | Time Required for Water to Soak in (min.) After Baking | Time Required for Water to Soak in (min.) | |
|---------------|--|--|------------|
| | | After Standing at Room Temperature | for 6 Days |
| 10 | 1.2 | 75 | |
| 20 | 2.5 | 60 | |
| 30 | 12.0 | 80 | |
| 40 | 30.0 | 180 | |
| 50 | 65.0 | 180 | |
| 60 | 80.0 | 180 | |

The following example will illustrate the degree to which the polyisocyanate tends to be bound to the leather.

EXAMPLE 8

2.002 grams of leather were immersed in 100% dimethyl isocyanate for a period of ten minutes. The leather was removed and found to have a drained weight of 2.865 grams indicating that it had picked up 0.863 grams of dimethyl isocyanate. The impregnated leather was placed in an air-circulating oven preheated to 100 C. for a period of 30 minutes. After curing, the leather was refluxed with 50 cc. of hexane for 1 hour after which the hexane was removed by evaporation. The leather then weighed 2.067 grams, indicating that approximately 0.065 grams of dimethyl isocyanate had reacted with the leather. The leather, after removal of the excess polyisocyanate, had water proofing characteristics similar to the products of Examples 6 and 7.

EXAMPLE 9

Cotton twill and 65/35% by weight polyester/cotton swatches were treated in a bath for one minute and wrung out using a hand wringer. The swatches were dried for ten minutes in an oven at 110° C. After drying, the swatches were washed five times in household detergent and then tested for tear strength and wrinkle recovery. The results are shown in the following table.

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| Treatment | Tear Strength (Warp) | | Wrinkle Recovery (Warp) | |
|------------------------------------|-------------------------|----------|----------------------------|----------|
| | 0 Washes | 5 Washes | 0 Washes | 5 Washes |
| Cotton Twill | | | | |
| No treatment—no washing | 1600 | 1632 | 54 | 52 |
| 1% Dimethyl isocyanate | 1899 | 2060 | 112 | 125 |
| 5% Dimethyl isocyanate | 1998 | 1980 | 111 | 131 |
| Control—distilled water and washed | 1354 | 1322 | 70 | 70 |
| Polyester/Cotton 65/35 | | | | |
| No treatment—no washing | 3170 | 3135 | 131 | 128 |
| 1% Dimethyl isocyanate | — | 2575 | 135 | 134 |
| 5% Dimethyl isocyanate | — | 2863 | 143 | 135 |
| Control—distilled water and washed | 2502 | 1952 | 120 | 119 |

This table shows that all treatments on both cotton twill and polyester/cotton show an improvement in wrinkle recovery coupled with an improvement in tear strength.

EXAMPLE 10

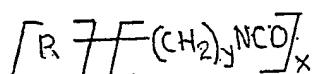
5 Cotton duck swatches one square yard in size were prewashed in an automatic washer using a common household detergent and were given an extra rinse to make sure that all residual detergent was removed. One swatch was impregnated for three minutes in a five percent dimethyl isocyanate emulsion after which the 10 swatch was wrung out to the point where it retained 85 to 90% of the emulsion based on

the dry weight of the swatch. The swatch was then dried for 45 minutes in a forced-air oven at 100° C. setting. The treated swatch was then rinsed in an automatic washer and again dried in the forced-air oven. This swatch, along with a swatch which was pre-washed only, was subjected to soil burial tests which consisted of eighteen days burial in sealed polyethylene bags. Tensile strength tests were then run with 15 20 the following results:

| Treatment | Average Tensile Strength in pounds |
|--|------------------------------------|
| Cotton duck—no treatment — not buried | 125 |
| Cotton duck — prewashed only | 38 |
| Cotton duck —treated with dimethyl isocyanate emulsion | 68 |

WHAT WE CLAIM IS:—

25 1. A process of treating a fibrous material which comprises contacting the fibrous material with a compound having the formula:



where y is 0 or 1, x is 2, 3 or 4 and R is the

hydrocarbon radical of a polymeric fat acid, as herein defined.

30 2. A process as claimed in claim 1 wherein y is 0 and x is 2.

3. A process as claimed in claim 1 wherein y is 1 and x is 2.

35 4. A process as claimed in any one of the preceding claims in which the isocyanate is employed in a concentration of 0.1% to 10% based on the weight of the fibrous material.

5. A process as claimed in claim 4 wherein said concentration is from 1% to 5%. 30

6. A process as claimed in any one of claims 1 to 5 in which the isocyanate is employed in the form of a solution in an organic solvent. 35

7. A process as claimed in claim 6 wherein the organic solvent is benzene, toluene, hexane or heptane.

8. A process as claimed in any one of claims 1 to 5 in which the isocyanate is employed in the form of an aqueous emulsion.

9. A process as claimed in any one of the preceding claims in which the fat acid providing the hydrocarbon fat radical is an ethylenically unsaturated acid.

10. A process as claimed in claim 9 in which the fat acid providing the hydrocarbon fat radical is oleic or linoleic acid.

11. A process as claimed in any one of the preceding claims wherein the fibrous material is contacted with the compound by immersion, brushing or spraying.

12. A process as claimed in any one of the preceding claims wherein the fibrous material is a cellulosic material.

13. A process as claimed in claim 12 wherein the cellulosic material is cotton.

14. A process as claimed in claim 12 wherein the cellulosic material is paper.

15. A process as claimed in any one of claims 1 to 11 in which the fibrous material is wool.

16. A process as claimed in any one of claims 1 to 11 in which the fibrous material is a mixture of cotton and polyester fibre.

17. A modification of a process as claimed in any one of claims 1 to 11 in which leather is treated in place of the fibrous material.

18. A process as claimed in claim 17 in which the leather is derived from cow hide, pig skin, goat skin or horse hide.

19. A process as claimed in claim 17 or claim 18 wherein the isocyanate is employed in a concentration of from 1/4% to 5% based on the weight of the leather.

20. A process as claimed in claim 1 or claim 17 substantially as herein described.

21. A process as claimed in claim 1 or claim 17 substantially as herein described with reference to the foregoing Examples.

22. A fibrous material or leather whenever treated by a process as claimed in any one of the preceding claims.

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